# THE OH STRETCHING BANDS OF ALCOHOLS IN NON-POLAR SOLVENTS

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Lieutenant Commander, United States Navy

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the requirements for the degree of

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# ABSTRACT

Dilute solutions of n-propyl alcohol in non-polar solvents (carbon tetrachloride, tetrachloroethylene, and carbon disulfide) have been studied by IR spectrophotometric analysis. Variation of the absolute intensities of monomeric and polymeric OH bands with increasing concentration at 25°C was observed. Within the concentration range studied (0.04 - 0.29M) the principal polymer formed in $CCl_4$ solutions was dimeric; in $C_2Cl_4$ and $CS_2$ solutions the principal polymer was trimeric. Equilibrium constants have been calculated for the monomer-polymer reaction in each solvent.

The writer wishes to acknowledge his indebtedness to Dr. John W. Schultz of the U. S. Naval Postgraduate School for his encouragement and invaluable assistance during the course of this study.

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# I. INTRODUCTION

## 1. The Hydrogen Bond.

Since its first suggestion over fifty years ago by Werner and by Moore and Winmill, and the subsequent recognition of its importance by Latimer and Rodebush in 1920, the hydrogen bond has assumed an ever-expanding role in scientific literature. Well it should, for continued analysis has revealed an increasing number of molecules which contain hydrogen bonds, many of which are important to biology and physiology, and chief of which is water. This relatively weak bond of about 2 to 10 kilocalories per mole offers an explanation for many properties of substances at room temperature. For example: hydrogen bonds restrain protein molecules to their native configurations; they explain the abnormally high dielectric constants of highly associated liquids such as water and hydrogen fluoride; they account for small ionization of ammonium hydroxide and for the formation of double molecules by acetic acid (1).

The widest general class of H-bonding concerns molecules of the same or of different substances, linked together in an intermolecular couple or chain. There can also be intramolecular bonding, chelation, wherein the bond is formed between groups in a single molecule such as a protein. In each instance there is (a) a proton donor such as an hydroxyl, carboxyl, amine or amide group, and (b) an electron donor, a basic group. Perhaps the most general operational definition of a hydrogen bond can be stated as follows:

"An H-bond exists between a functional group A -- H and an atom or group of atoms B in the same or a different molecule when

(a) there is evidence of bond formation (association or chelation)

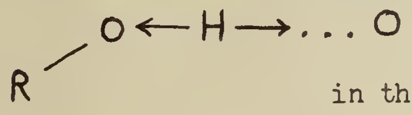
(b) there is evidence that this new bond linking A -- and B specifically involves the hydrogen atom already bonded to A." (2)

This definition covers the manifold criteria specified by other authors for detection of bonding by crystallographic or spectroscopic means or by using other procedures of physical chemistry (3). Most significantly it does specify that the H atom of the original molecule must be affected in a new bond with an electron donor.

## 2. Infrared Spectroscopy

Infrared spectroscopy has been an invaluable tool in H-bond research since the 1930's. Since infrared spectra reveal characteristic frequencies of molecular vibrations, and vibrational spectra are markedly disturbed by hydrogen bond formation, these spectra can provide a significant means of identification of the H-bond in accordance with the definition heretofore specified. The molecular vibrations are dependent upon molecular geometry, charges and forces which maintain equilibrium, and masses of the vibrating atoms, therefore many physical properties of the molecule can be deduced by interpretation of the characteristic frequencies and band intensities exhibited in an infrared spectrum.

Vibrations of the molecule occur in several modes: in-plane stretching, in-plane bending, and out-of-plane torsion. Easily the most prominent of these modes is in-phase stretching, which can be illustrated as



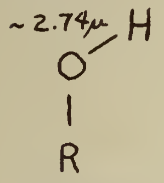
in the case of an alcohol ROH, whose characteristic stretching frequency $\nu_s$ would be in the range 4000 to 3000cm$^{-1}$.

Early studies of alcohols performed during the 1930's by Freymann (4), Errera and Mollet (5), and Fox and Martin (6,7) showed the effect of changing the concentration of alcohol solutions. Solutions being the most convenient method of IR study, carbon tetrachloride or some other non-polar liquid was chosen as the solvent in order to avoid the formation of complexes and interference with intra-or intermolecular bonding. In the case of ethyl alcohol, for example, Errera and Mollet reported that with increasing concentration not only did the characteristic frequency decrease, but the sharp absorption peak found at 3640 $cm^{-1}$ for extremely dilute solutions decreased in size while a broad band at 3350 $cm^{-1}$ rapidly intensified. Freymann (4), Errera, Gaspart and Sack (8), and Wulf and Liddel (9) found that intensity and frequency of alcohol solutions were greatly affected by temperature as well as by concentration. With increasing temperature, frequency increased, and a major decrease in absorption was observed in the broad absorption band especially.

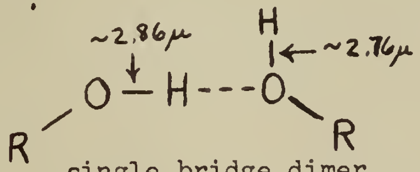
### 3. Types of Bonding

Widespread interest in the spectrographic study of the hydrogen bond engendered a great deal of speculation as to the meaning of the absorption peaks, which appeared characteristic of innumerable alcohols investigated, both aliphatic and aromatic. It became customary to refer to the very sharp peak at highest fundamental stretching frequency as that of the "free OH bond" or the "monomer" peak. At slightly lower frequency, about 150 $cm^{-1}$ lower, usually a small broad peak called the "dimer" band could be seen developing as concentration of the solution increased. Soon, however, as concentration was raised, a broad band extending from 3600 $cm^{-1}$ to 3000 $cm^{-1}$ and centered about 3300 $cm^{-1}$ emerged and dominated the

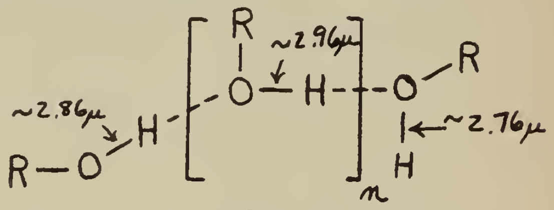
spectrum. This wide band became known as the "associated" or "polymeric" region. After carrying out measurements for a long series of alcohols in the $3\mu$ region Kuhn (10) established that in all cases (except methanol) the sharp, free OH band was found to be between 3644 and 3605 cm$^{-1}$. Low concentrations and long pathlengths enabled him to view only the monomeric and dimeric bands, however. Kinsey and Ellis (11) reported a spectrographic study of aliphatic alcohols both pure and in solution. It was noteworthy that even in pure liquid a small sharp band of monomer remained. Smith and Creitz (12) offered an explanation of a broad spectrum of molecules bonded in variable amounts, thus accounting for the wide association band as a composite of sharper peaks. Their research also gave evidence of a single-bridge dimer to account for the middle frequency peak. Their models for the bonded molecules were as follows:



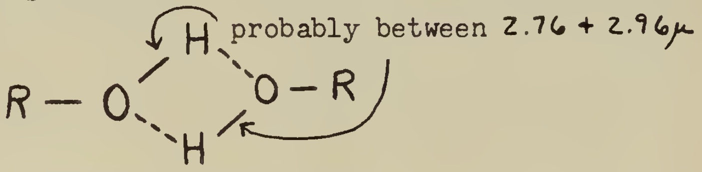
monomer



single bridge dimer



polymer



double bridge dimer

Temperature effects on the intensity of alcohols and phenols and on the frequency shifts were studied by Hughes, Martin and Coggeshall (13), and by Finch and Lippincott (14). The former theorized that a rise in temperature decreased the force field exerted by a molecule on its neighbors by increasing the average distance between molecules. Finch and Lippincott interpreted their data in terms of a potential function model

of H-bonding. Their explanation of temperature shifts of OH frequencies in alcohols was based upon a Boltzmann distribution of H-bond energies resulting from excitation of the O....O mode of vibration to higher energy levels. Lippincott (15) also proposed a simple one-dimensional model for hydrogen bonding, based upon the potential function $V = D\left[1 - \exp\left(\frac{-n\Delta r^2}{2r}\right)\right]$ where D represented bond dissociation energy and r the bond distance. Through application of conditions of stable equilibrium he obtained relations which permitted calculation of OH frequency shifts, bond distances, H-bond energies and $k_{O....O}$ force constants, all as functions of the O....O distance. The relationship between H-bonding and O....O distance was believed by Rundle and Parasol (16) to be direct. They showed that symmetric OH....O bonding gives longer OH distance and higher frequency and that the converse is true for asymmetric bonding. Recently Feilchenfeld (17) has proposed a formula for relating OH bond length, bond energy, and O....O bond distance:

$$E + E' = k\left[\frac{1}{L^3_{O-H}} + \frac{1}{L^3_{H\ldots O}}\right] = k\left[\frac{1}{L^3_{O-H}} + \frac{1}{(L_{O\ldots O} - L_{O-H})^3}\right]$$

where E is O--H bond energy, E  is H....O bond energy, k = 96.7 Å$^3$ kcal/mole, and L is bond length.

Solvent effects have been studied by Pullin (18), who believes the most important feature of non-polar solvents to be dipole-induced dipole and dispersion forces in the absence of strongly orientation-dependent forces such as H-bonding. The former forces can be approximated by considering the solute molecule to be within a spherical cavity in a uniform dielectric. Previously (1940) Buswell, Downing, and Rodebush (19)

theorized that an increase in molar absorption coefficient was accounted for by the increase in dipole moment with increasing dielectric constant of the environment.

The majority of chemists have utilized the electrostatic model of the hydrogen bond which employs a specific potential function as the relation between bonded atoms. A "Morse function" was used by Coggeshall (23) to calculate absorption intensity. He solved the Schrödinger equation by adding a term expressing polarization energy of an OH group due to the electrostatic interaction. Thus he obtained reasonable agreement between calculated and observed intensities. Unfortunately Coggeshall's ratio of the squares of matrix elements of the dipole moment for H-bonded and free bonds was subsequently proved by Francis (24) to be in error. Coggeshall mistakenly assumed the absorption peaks to be Lorentzian curves, whereas they are not at all identically shaped. Barrow (25) has performed experiments with dilute alcohol solutions to prove that the stretching vibration of the OH bond is the beginning of ionization -- whence the term "ionic character" for this model. Using integrated absorption intensities, Barrow was able adequately to correlate the change in the molecular dipole moment with the percent ionic character of the OH bond and the OH bond distance.

The entirely electrostatic model of the H-bond with fixed charges resting upon the atoms has been challenged in recent years by the quantum theory of charge transfer. Such a theory has been proposed and developed by Tsubomura (20, 21). He assumed a partial electron transfer from the lone pair orbital of the proton acceptor to the OH orbital of the proton donor, or ($X -- O^{-}H -- Y^{+}$) to ($X -- O -- H \dots Y$). Tsubomura's studies

were of ternary systems of alcohol, proton acceptor, and a solvent, usually $CCl_4$. The concentration of the H-bond complex was calculated, and the value of an equilibrium constant $K$ could then be found. This constant was found to be closely related to H-bond energy, though not strictly related to $\Delta \nu_s$. IR intensity is directly proportional to H-bond energy, however. Additional work by Tsubomura with phenol produced two proofs that the sign of the change of dipole moment $\frac{\partial \mu_0}{\partial r}$ is positive in the intermolecular H-bond. Huggins and Pimentel (22) have agreed that Tsubomura's model may be more closely allied to experimental evidence than is Barrow's "ionic character" model of the hydrogen bond.

## 4. Definition of terms

The pronounced changes in absorption intensity with hydrogen bonding were increasingly subject to analysis as scientists probed the secrets of the chemical bond. Therefore a uniform system for experimental determination of intensities was devised. The fundamental law governing the absorption in solution of monochromatic light: $I = I_0 \exp(-K_\nu CL)$ was converted to an absorption coefficient $K_\nu = \frac{1}{CL} \ln \frac{I_0}{I}$ where $I_0$ is incident intensity, and $I$ is the light transmitted by a cell of length $L$ centimeters containing a solution of concentration $C$ moles/liter. For many purposes the molecular extinction coefficient $\epsilon = \frac{1}{CL} \log_{10} \frac{I_0}{I}$ is used. These relationships are commonly referred to as Beer's Law (26).

A most precise plot of an IR absorption band is optical density $d$ against frequency $\nu$. Optical density can be defined as being equal to $\log_{10} \frac{I_0}{I}$, or $\epsilon CL$. Thus the area beneath the plot of $d$ versus $\nu$

gives the area $\int d \, d\nu$ or $\int \epsilon CL \, d\nu$. In order to obtain an absolute (or integrated) absorption intensity A, the area beneath the optical density curve is plotted against concentration times pathlength. The slope of the curve therefrom is $\frac{\int \epsilon CL \, d\nu}{CL} = \int \epsilon \, d\nu$. Absolute absorption intensity is equal to $\int K_\nu \, d\nu = 2.303 \int \epsilon \, d\nu = 2.303 \text{ X slope}$.

The units of absolute intensity are: $\dfrac{\text{cm}^{-1}}{\frac{\text{moles}}{\text{liter}} \text{ x cm}}$.

## II. EXPERIMENTAL

### 1. Preparation of solutions

Solutions of n-propyl alcohol in non-polar solvents carbon tetrachloride, tetrachloroethylene, and carbon disulfide were prepared by weighing the alcohol to the nearest $10^{-4}$ gram in a 100 ml volumetric flask on an analytical balance. Solvent was added to the alcohol in the flask, directly from the bottle, and filled up to the mark.

Reagent grade carbon tetrachloride and carbon disulfide from Allied Chemical Company, and spectro grade tetrachloroethylene from Eastman Organic Chemicals were used as solvents. In every instance a previously unopened bottle of solvent was used for preparation of solutions. No significant impurities were noted in any of these solvents in the IR region studied, even at pathlengths as long as 0.3500 cm. Purity of the alcohol (Eastman Organic Chemicals) was determined by use of the Perkin-Elmer vapor fractometer Model 154. Only one impurity was detected, and it was found to be of no consequence inasmuch as the band of the alcohol fraction was 150 times as intense as that of the impurity.

In order to determine the volatility of a dilute (0.1396M) solution of n-propyl alcohol and carbon tetrachloride, again the vapor fractometer was used. It was shown that composition of the solution remained unchanged (a) when kept in a glass-stoppered volumetric flask, and (b) when transferred from a cell that had been used to obtain infrared spectra, provided samples were taken directly from the volumetric flask. A standard 10 microliter sample for each of the following cases was analyzed: (1) fresh solution taken directly from stoppered flask, (2) solution which had remained in the glass stoppered volumetric flask

for 14 days, (3) two-week-old solution which had been used for a spectrographic analysis, the IR sample having been taken directly from the stoppered volumetric and the fractometric sample taken directly from the IR test cell, (4) solution that had been allowed to stand for 15 minutes in an uncovered beaker, (5) solution that had been aerated by transferring between 50 ml beakers at least six times, (6) aerated solution that had been allowed to stand for 15 minutes in an uncovered beaker. The maximum error from original composition was found to be 1.45% if the solution were taken from stoppered volumetric or stoppered IR cell. The error was 4.48% when the solution was allowed to stand uncovered, and it increased to 15.75% after aeration and standing. Since inaccuracies of the fractometer and in estimation of areas on the chromatograph may well account for 3% error, it is apparent that the solution was not so volatile as to preclude obtaining accurate, reproducible results.

### 2. Obtaining spectrophotometric data

All spectra were obtained using a Perkin-Elmer double beam spectrophotometer, Model 221 with NaCl prism-grating interchange. A variable pathlength cell (Research and Industrial Instruments Company) with NaCl windows was used to contain the sample, which was inserted by means of a hypodermic syringe. Reproducibility of pathlength setting was ±0.2 micron and zero-setting was calculated to be 0.0462 cm, using the interference fringe pattern to find the cell zero. Variable spacing permitted selection of pathlengths to 0.5500 cm. Teflon stoppers were used on the cell itself. Exposure of the solution to the atmosphere was minimized by keeping the volumetric flask tightly stoppered unless actually withdrawing a sample

from it with the syringe.

Pathlength to be used for a specific alcohol solution was selected on the basis of peak absorption intensities of the OH band. An optimum pathlength produced a measurable polymeric stretching region while the monomeric peak did not exceed 65% absorption. The basic pathlength, however, was 0.0500 cm. Only the most dilute solutions were studied at greater than 0.0500 cm and none were examined at shorter pathlengths.

Prior to each run, the empty cell was inserted into the holder on the instrument for about 15 minutes with the beam shining through its windows. This brought the metal cell to a nearly constant temperature. The ultimate cell temperature during a run was 25°C, and the average temperature of the air-conditioned laboratory was 21°C. In obtaining a spectrum for a solution of known concentration the spectrophotometer was set with a 927 slit program, drum speed of 2.5 cm per minute, and attenuator speed of 11:00. A scale of 25 wavenumbers per cm of chart paper was chosen. The zero transmittance line was traced and adjusted actually to read zero on the chart paper.

The filled cell was always allowed to remain in the instrument holder for about two minutes in order to equalize cell-liquid temperatures. A background spectrum of solvent only, as well as a spectrum for the solution, was traced for the region studied (3900-2800 wavenumbers). Thus a single run consisted of the zero line, the solvent background spectrum, and the solution spectrum. Prior to each refill of the cell, it was thoroughly dried and flushed with air forced through it by hand bulb. Three complete runs were made for a given solution, and for each run a new sample of solution was drawn from the volumetric flask.

### 3. Plotting data

At ten $\mathrm{cm}^{-1}$ intervals in the region studied, background absorption intensity of the solvent ($I_o$) and absorption intensity of the solution ($I$) were recorded. Estimates of the overlapping portions of the monomeric OH band with that of the polymeric band were sketched in, giving consideration to symmetry, and an estimate of the end of the polymeric OH band was made also where it overlapped the CH band. At each frequency the ratio $I_o/I$ was calculated by slide-rule. Then a smooth plot of log $I_o/I$ (optical density) versus frequency was made.

The areas under each peak, representing $\int d \; d\nu$ or $\int \epsilon CL \; d\nu$ were determined by graphical integration, measurements being repeated until successive readings agreed to within 1%. Then the values of $\int d \; d\nu \, (\mathrm{cm}^{-1})$ were plotted against concentration times pathlength ( $\frac{\text{moles}}{\text{liter}}$ x cm). Another presentation of data shows $2.303 \int d \; d\nu$ versus mole percentage of n-propyl alcohol in solution. Each point on these curves is the result of an average of at least three separate determinations. The intensities are considered to be reliable to better than 10% accuracy.

## III. RESULTS AND DISCUSSION

The dilute solutions of n-propyl alcohol in carbon tetrachloride, tetrachloroethylene, and carbon disulfide which were studied are listed in Table I. No attempt was made to prepare solutions of identical molarity for each solvent, however the solutions were prepared in an approximately regular progression of increasing concentration.

Table I

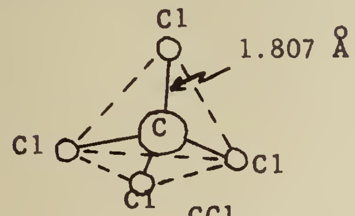
| Molar concentration | $\frac{\text{Solvent}}{\text{Alcohol}}$ mole ratio | Mole %, alcohol |
|---|---|---|
| $CCl_4$ solutions of n-propyl alcohol | | |
| 0.0454 | 227.5 | 0.44 |
| 0.0879 | 117.2 | 0.85 |
| 0.1396 | 73.53 | 1.34 |
| 0.1872 | 54.57 | 1.80 |
| 0.2253 | 45.21 | 2.16 |
| 0.2631 | 38.64 | 2.52 |
| $C_2Cl_4$ solutions | | |
| 0.0413 | 237.2 | 0.42 |
| 0.0967 | 101.03 | 0.98 |
| 0.1334 | 72.99 | 1.35 |
| 0.1825 | 53.08 | 1.85 |
| 0.2418 | 39.96 | 2.44 |
| 0.2884 | 33.42 | 2.91 |
| $CS_2$ solutions | | |
| 0.0435 | 379.5 | 0.26 |
| 0.0926 | 177.8 | 0.56 |
| 0.1339 | 122.7 | 0.81 |
| 0.1909 | 85.60 | 1.15 |
| 0.2342 | 69.59 | 1.42 |
| 0.2738 | 59.38 | 1.66 |

Variation of intensity, or more specifically, variation of transmittance with increasing concentration is shown in Figure 1, which is a

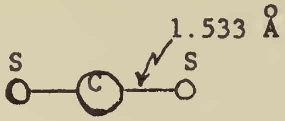
composite of the spectra obtained from solutions of $CCl_4$. The most striking feature of this comparison is the quite sudden and overpowering development of the polymeric band with increasing concentration of the alcohol solution. The peak frequency of this polymeric band is 3350 $cm^{-1}$, and it extends from 3600 to 3050 $cm^{-1}$. A tentative peak at 3505 $cm^{-1}$ is discernible at very low concentrations, and indeed its effect remains as a modification to the broad polymeric band even at the highest concentrations studied. A steady decrease in the intensity of the monomeric peak at 3632 $cm^{-1}$ accompanies the increase in concentration. There is no evidence of a shift in monomer peak frequency with change in concentration. The same effect of increasing concentration is noted in spectra of solutions of $C_2Cl_4$ and $CS_2$, but to avoid redundancy their composite spectra are not shown.

These results, upon cursory inspection, give the distinct impression that with increasing concentration of the alcohol solution some interaction is causing diminution of the momomeric species of the alcohol. Conceivably at almost infinitely dilute solution only the monomeric band can be distinguished, and this has in fact been proven by Liddel and Becker (27) and other investigators. As concentration of the solution increases, a decrease in monomeric peak height together with beginnings of a small peak at 3505 $cm^{-1}$ indicates that polymerization through hydrogen bonding has begun. Soon the much larger peak at 3350 $cm^{-1}$ starts to develop, signifying further polymerization of perhaps a different sort inasmuch as the vibrational frequency is quite different. It remains to be seen what these species of polymers could be.

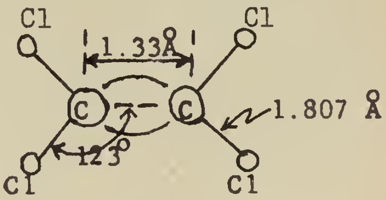
Next a comparison of the spectra of n-propyl alcohol solutions of similar molar concentration can be made. The spectra which are shown in Figure 2 are (a) 0.1396M in $CCl_4$ (b) 0.1334M in $C_2Cl_4$ and (c) 0.1339M in $CS_2$. Although the general shapes of the curves are similar, it is immediately apparent not only that the $CS_2$ solution has less monomeric intensity, but it has a monomeric peak frequency 12 $cm^{-1}$ less than solutions of $CCl_4$ and $C_2Cl_4$. Mecke (28) has stated that as a rule when changing from "indifferent" or non-polar solvents to solvents which promote stronger interaction, there will be a broadening of the stretching band with a decrease in peak intensity and a change to lower frequency. This indicates that carbon disulfide is more reactive with the alcohol than the other two solvents, since the monomer is affected more strongly and the O-H frequency has decreased due to this solvent effect. The fact that the $CS_2$ solution has a lesser monomeric peak frequency than $CCl_4$ and $C_2Cl_4$ solutions can be explained by application of an empirical formula developed by Pullin (18). His equation, utilizing the concept of a solute molecule within a cavity of solvent in a uniform dielectric, shows that the frequency of the stretching vibration of a molecule in liquid solution is decreased from the frequency of that molecule in gaseous form by an amount indirectly proportional to the volume of a *solvent* molecule. According to Pauling (1) the models for solvents used are as follows:



$CCl_4$



$CS_2$



$C_2Cl_4$

Assuming each solvent molecule to be spherical, their order of increasing size would be $CS_2$, $CCl_4$, and $C_2Cl_4$. Thus $CS_2$ would show the largest decrease in frequency, as it does. Brown (29) has cautioned, however, that the geometrical character of the <u>solute</u> molecule is important in determining non-polar solvent effects and that the solvent effect for intensities does not always parallel that for frequencies.

Figure 3 shows more clearly the increase in maximum polymeric intensity with corresponding decrease in peak monomeric intensity for the $CS_2$ solution. Figure 3 is a plot of optical density versus frequency. It is noted in both plots that the polymeric peak height as well as the area under the curves is greater for $C_2Cl_4$ and $CS_2$ than for $CCl_4$ solution. Conceivably, greater polymerization takes place in $CS_2$ and $C_2Cl_4$ solutions, such polymerization being different from that of the $CCl_4$ solution. That $C_2Cl_4$ is more conducive to polymerization than $CCl_4$ is indicated by the fact that although this solution is of slightly lower concentration than the $CCl_4$ solution, a larger polymer band is produced.

Figure 4 is a plot of the area under the optical density curve against total molar concentration times pathlength. In other words it is a plot of the graphically integrated area $\int d \; d\nu = \int \epsilon CL \; d\nu$ versus $C \times L$, though only for the monomeric peak. Figure 5 is a similar plot for the graphically integrated area under the broad polymeric peak. Both figures utilize data from Table II. In the case of Figure 5, and referring back to Figure 3, the entire area other than the monomeric band was considered to constitute the polymeric band. No attempt was made to differentiate between dimer and polymer since such an approximation was deemed inadvisable due to large overlap of the bands. Although there is dimer

## TABLE II

| Molar concentration (moles/liter) | Pathlength (cm) | $\int \log_{10} \frac{I_0}{I} d\nu = \int d\, d\nu$ Monomer | $\int \log_{10} \frac{I_0}{I} d\nu = \int d\, d\nu$ Polymer ($cm^{-1}$) | $2.303 \int d\, d\nu$ Monomer | $2.303 \int d\, d\nu$ Polymer ($cm^{-1}$) |
|---|---|---|---|---|---|
| $CCl_4$ solutions | | | | | |
| 0.0454 | | 4.759 | 1.830 | 10.960 | 4.214 |
| 0.0879 | | 8.083 | 8.454 | 18.615 | 19.470 |
| 0.1396 | | 10.852 | 28.467 | 24.992 | 65.560 |
| 0.1872 | | 13.342 | 51.694 | 30.727 | 119.051 |
| 0.2253 | | 16.352 | 79.752 | 37.659 | 183.669 |
| 0.2631 | | 16.760 | 104.651 | 38.598 | 241.011 |
| $C_2Cl_4$ solutions | | | | | |
| 0.0413 | | 3.382 | 1.053 | 7.789 | 2.425 |
| 0.0967 | | 7.300 | 10.780 | 16.812 | 24.826 |
| 0.1334 | | 10.146 | 29.694 | 23.366 | 68.385 |
| 0.1825 | | 12.227 | 57.566 | 28.159 | 132.574 |
| 0.2418 | | 14.304 | 104.486 | 32.942 | 240.631 |
| 0.2884 | | 16.757 | 146.052 | 38.591 | 335.776 |
| $CS_2$ solutions | | | | | |
| 0.0435 | | 3.986 | 1.193 | 9.180 | 2.747 |
| 0.0926 | | 8.057 | 9.831 | 18.555 | 22.641 |
| 0.1339 | | 10.257 | 26.349 | 23.622 | 60.682 |
| 0.1909 | | 14.193 | 60.208 | 32.686 | 138.659 |
| 0.2342 | | 16.129 | 98.817 | 37.145 | 227.576 |
| 0.2738 | | 16.743 | 124.777 | 38.559 | 287.361 |

contribution throughout the concentration range studied, the polymer appears to be more important and the dimer is considered a portion of the polymer.

It is curious that monomeric band curves indicate a closer similarity between the $CCl_4$ and $C_2Cl_4$ solutions rather than between $C_2Cl_4$ and $CS_2$ solutions as might have been anticipated from Figure 3. At the higher concentrations studied, the monomer band sizes of the $CCl_4$ and $CS_2$ solutions and the slopes of the curves are nearly identical, which would indicate at least the same rate of polymerization of the alcohol in these solvents. Tetrachloroethylene solutions show a greater degree of polymerization and a greater rate, that is, a greater decrease in monomer with increasing concentration.

Study of Figure 5, however, indicates that up to a concentration of approximately 0.11M, alcohol in each of the three solutions polymerizes to the same degree and at the same rate. Above that concentration, $CS_2$ and $C_2Cl_4$ solutions polymerize more and faster than do $CCl_4$ solutions.

Other facets of the intermolecular hydrogen bonding which is taking place in these solutions are revealed by slightly different presentation of the data obtained by infrared spectrophotometry. Figures 6 and 7 are plots of $\int \ln_e \frac{I_o}{I} \, d\nu$ or $2.303 \int \epsilon CL \, d\nu$ versus the mole percentage of n-propyl alcohol in solution, using data from Tables I and II. Now it is obvious not only how much greater but how much faster is the polymerization of hydrogen bonding in $CS_2$ solution. It is surprising to find that polymerization begins and rapidly intensifies at such an extremely low alcoholic mole percentage as 0.3%. Expressed in other terms this

means that when more than three molecules of alcohol are present in a solution with 997 molecules of solvent, those alcohol molecules will find each other and begin to polymerize. This is remarkable indeed. When the alcohol population has increased to six parts per 1000, polymerization in $CS_2$ is nearly four times that which is taking place in $C_2Cl_4$ or $CCl_4$ solutions, assuming, of course, similar intensity for the polymeric band in all three solvents.

The absolute intensity of the monomer band for each solution is obtained by drawing the limiting slope as concentration approaches zero on the curves of Figure 4. This slope is equal to $\frac{\int \epsilon \, CL \, d\nu}{CL}$ or $\int \epsilon \, d\nu$ and must be multiplied by 2.303 to give A, the absolute intensity of the monomer. Had the assumption been valid that the monomeric band approximated a Lorentzian curve in every instance, these intensities could as well have been calculated from an equation attributed to Ramsey (30), utilizing the width at half-height of the monomer peak intensity:

$$A = \frac{\pi}{2} \left(\Delta\nu_{1/2}\right) \frac{\ln_e \frac{I_0}{I}}{CL} \qquad \left( \frac{cm^{-1}}{\frac{moles}{liter} \times cm} \right)$$

where $\Delta\nu_{1/2}$ is the width at half-height measured in $cm^{-1}$ and other factors as are heretofore defined. Tsubomura (21) plotted absolute intensity versus peak frequency for many solutions, having computed A with Ramsey's formula. The absolute intensities computed from the limiting slopes of Figure 4 all can be plotted on or very near the smooth curve plotted by Tsubomura. Table III lists the absolute intensities obtained by this work using the slopes of curves plotted after graphical integration of the monomer band. It also shows the absolute intensities obtained

utilizing width at half-height data. Except for the tetrachloroethylene solutions, apparently the assumption that the monomeric band is a Lorentzian curve is valid.

TABLE III

| Solvent | Absolute intensity by graphical determination | Absolute intensity by formula |
|---|---|---|
| $CCl_4$ | $0.520 \times 10^4$ | $0.520 \times 10^4$ |
| $C_2Cl_4$ | $0.389 \times 10^4$ | $0.518 \times 10^4$ |
| $CS_2$ | $0.460 \times 10^4$ | $0.450 \times 10^4$ |

When absolute intensity of the monomer for each of the solutions has been found, a relationship is established as follows:

$$A = \frac{2.303 \int d \; d\nu}{C_m \; L}$$

where $C_m$ represents the concentration of monomeric species in solution. Since <u>A</u> is a constant, and $2.303 \int d \; d\nu$ is known for each of the solutions, concentration of the monomer can be determined by: $C_m = \frac{2.303 \int d \; d\nu}{A \; L}$.

The molar concentration of n-polymer in solution ($C_{pn}$) will be equal to $\frac{C - C_m}{2}$ if the polymer is a dimer, to $\frac{C - C_m}{3}$ if the polymer is a trimer, to $\frac{C - C_m}{4}$ if it is a tetramer, etc. Table IV gives the results of these calculations.

If $K_{1n} = \frac{C_{pn}}{C_m^{\,n}}$ represents the equilibrium constant which can be determined if there is an equilibrium between the monomeric species and

## TABLE IV

| Total Molar Conc. (mole/liter) | $2.303 \int d\, d\nu$ (cm$^{-1}$) | $C_m$ (mole/l) | $C_m^{\ 2}$ $10^{-3}$ | $C_m^{\ 3}$ $10^{-4}$ | $C_m^{\ 4}$ $10^{-4}$ | $C_{p2}$ $10^{-2}$ | $C_{p3}$ $10^{-2}$ | $C_{p4}$ $10^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| $CCl_4$ solutions | | | | | | | | |
| 0.0454 | 10.960 | .0422 | 1.78 | .75 | .032 | .16 | .11 | .08 |
| 0.0879 | 18.615 | .0716 | 5.13 | 3.67 | .263 | .82 | .54 | .41 |
| 0.1396 | 24.992 | .0961 | 9.24 | 8.88 | .854 | 2.18 | 1.45 | 1.09 |
| 0.1872 | 30.727 | .1182 | 13.97 | 16.50 | 1.950 | 3.45 | 2.30 | 1.75 |
| 0.2253 | 37.659 | .1448 | 21.00 | 30.40 | 4.410 | 4.02 | 2.68 | 2.01 |
| 0.2631 | 38.592 | .1484 | 22.00 | 32.60 | 4.840 | 5.74 | 3.82 | 2.87 |
| $C_2Cl_4$ solutions | | | | | | | | |
| 0.0413 | 7.789 | .0400 | 1.60 | .64 | .026 | .06 | .04 | .03 |
| 0.0967 | 16.812 | .0864 | 7.47 | 6.45 | .558 | .52 | .34 | .26 |
| 0.1334 | 23.366 | .1201 | 14.43 | 17.33 | 2.082 | .66 | .44 | .33 |
| 0.1825 | 28.159 | .1448 | 20.96 | 30.35 | 4.390 | 1.88 | 1.26 | .94 |
| 0.2418 | 32.942 | .1694 | 28.68 | 48.58 | 8.230 | 3.62 | 2.41 | 1.81 |
| 0.2884 | 38.591 | .1980 | 39.20 | 61.22 | 15.370 | 4.52 | 3.01 | 2.26 |
| $CS_2$ solutions | | | | | | | | |
| 0.0435 | 9.180 | .0399 | 1.59 | .63 | .025 | .18 | .12 | .09 |
| 0.0926 | 18.555 | .0807 | 6.51 | 5.25 | .424 | .60 | .40 | .30 |
| 0.1339 | 23.622 | .1027 | 15.50 | 15.92 | 2.400 | 1.56 | 1.04 | .78 |
| 0.1909 | 32.686 | .1421 | 20.20 | 28.64 | 4.080 | 2.44 | 1.63 | 1.22 |
| 0.2342 | 37.145 | .1615 | 26.10 | 42.15 | 6.81 | 3.64 | 2.42 | 1.82 |
| 0.2738 | 38.559 | .1676 | 28.10 | 47.10 | 7.90 | 5.31 | 3.54 | 2.66 |

the principal polymeric species formed, a plot of $C_{pn}$ against $C_m^n$ will yield a straight line. Figure 8 is a plot of monomer-dimer equilibrium relationships; Figure 9 is a plot of monomer-trimer equilibrium relationships; and Figure 10 is a plot of monomer-tetramer relationships. The best straight lines can be drawn for monomer-dimer equilibrium in $CCl_4$ solutions, and for monomer-trimer equilibria in $C_2Cl_4$ and $CS_2$ solutions. The slopes of these lines are determined to be:

$CCl_4$ : $K_{12} = 2.2$
$C_2Cl_4$ : $K_{13} = 4.6$
$CS_2$ : $K_{13} = 6.1$

While Mecke (28) and others state that there are practically no dimeric molecules for alcohols but that the trimer is the lowest polymeric form in solution, Smith and Creitz (12) and Liddel and Becker (27) dispute this with proofs that alcohol dimers do exist in $CCl_4$. Both Liddel and Smith aver that an open dimer with a non-bonded H would probably contribute to the monomer band, since in all liklihood the vibrational frequency of this non-bonded H would be quite near to the monomer peak frequency. Thus an open, or single-bridge dimer would simply magnify one side of the monomer peak, altering it slightly from the Lorentzian form. Figure 1 shows that the monomer peaks are not exactly symmetrical. The single-bridge dimer could be the explanation for the slight bulge on the low frequency side of the peak. Liddel concerned himself primarily with the 3500 $cm^{-1}$ region, however, in proving the existence of cyclic dimers. Using temperature data he was able to determine $\Delta H$ for formation of the polymer, which was nearly double that for a single OH...O bond. Thus he deduced that this band consisted of cyclic dimers.

Having identified the peak which appears in all solutions at 3505 $cm^{-1}$ as that of a cyclic dimer and adducing the small asymmetry of the monomer peak to be due to open dimers, it may seem incompatible then to adjudge the equilibrium constant $K_{12}$ for $CCl_4$-alcohol solutions to be that between monomer and dimer. The main polymer peak is developed at 3350 $cm^{-1}$, indicating that a polymeric species other than dimeric is present. Yet the only straight-line relationship in alcohol-$CCl_4$ solutions is between monomer and dimer. Possibly, the magnitude of the dimer band at 3505 $cm^{-1}$ is sufficiently great to represent the principal polymeric species, rather than the only polymeric species present within the range of concentrations studied. The monomer-trimer equilibria established for $C_2Cl_4$ and $CS_2$ solutions of alcohol agree in principle with other published research, although no specific data on such equilibria are available for n-propyl alcohol solutions.

The unique and anomalous behavior of $C_2Cl_4$ solutions in particular and the irreconcilable discrepancies in this work portend further valuable and interesting research in this field.

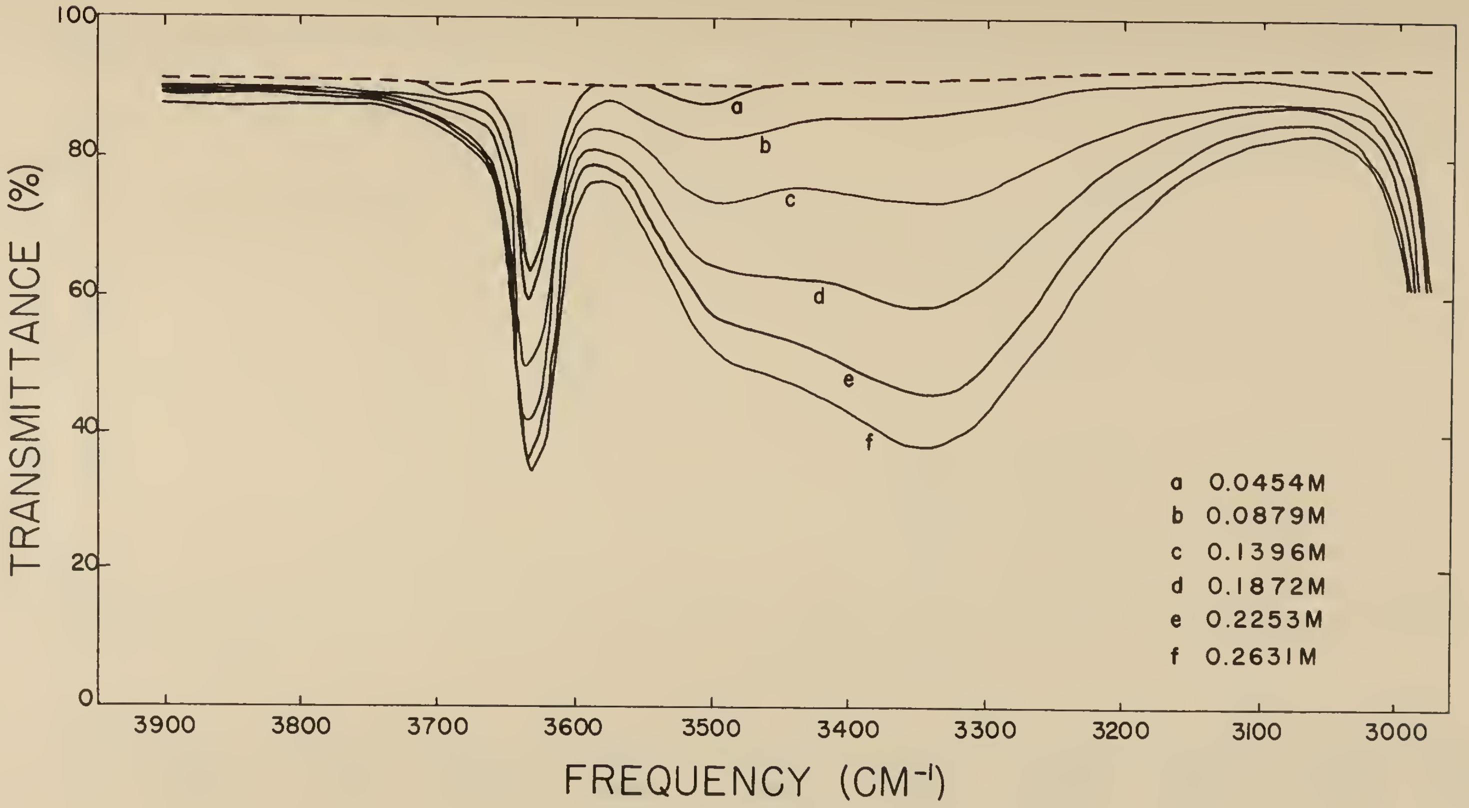


Figure I

Infrared Spectra of Solutions of n-propyl Alcohol in Carbon Tetrachloride

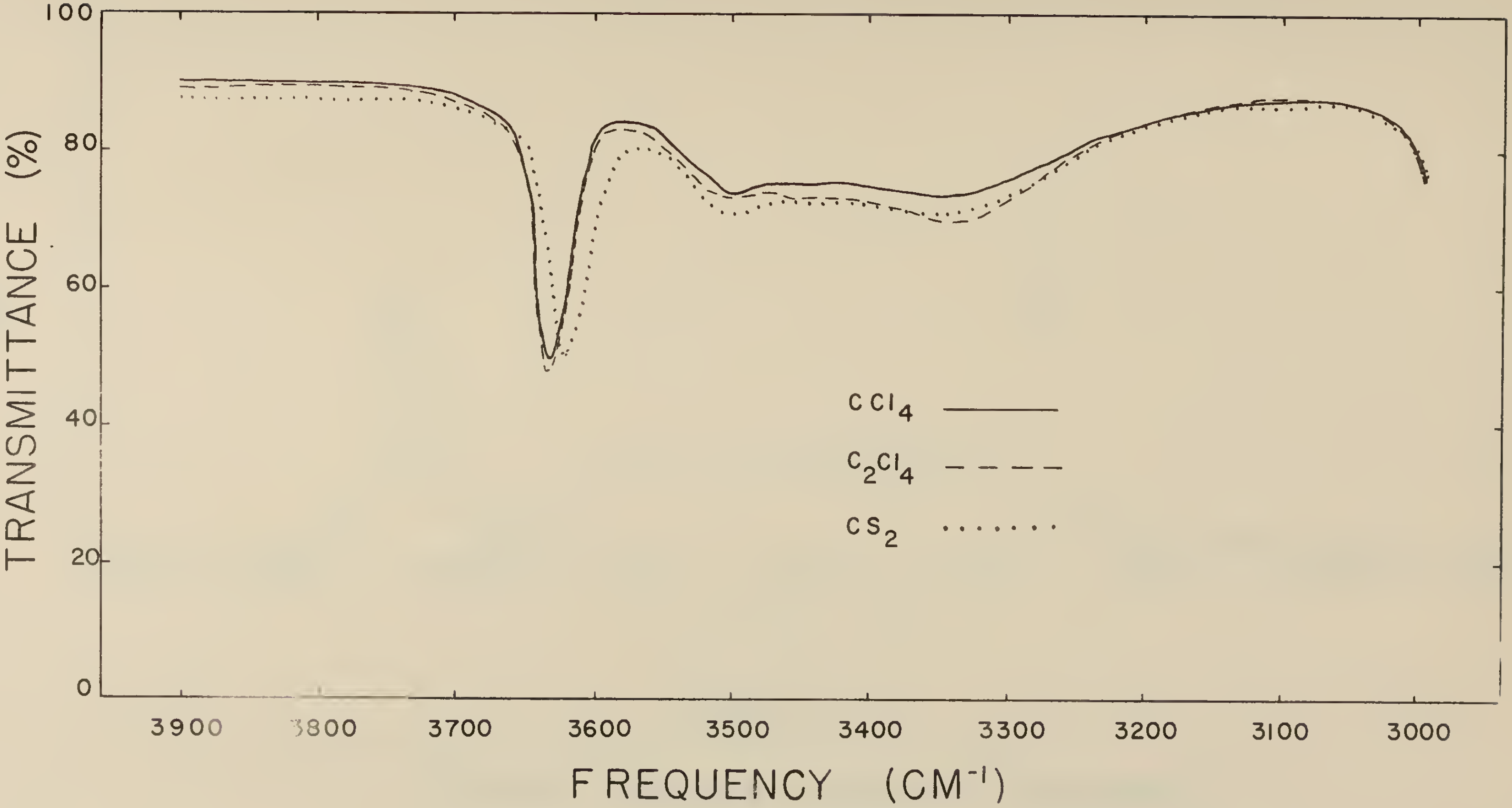


Figure 2

Infrared Spectra of n-propyl Alcohol in $CCl_4$, $C_2Cl_4$, and $CS_2$ at Similar Concentration

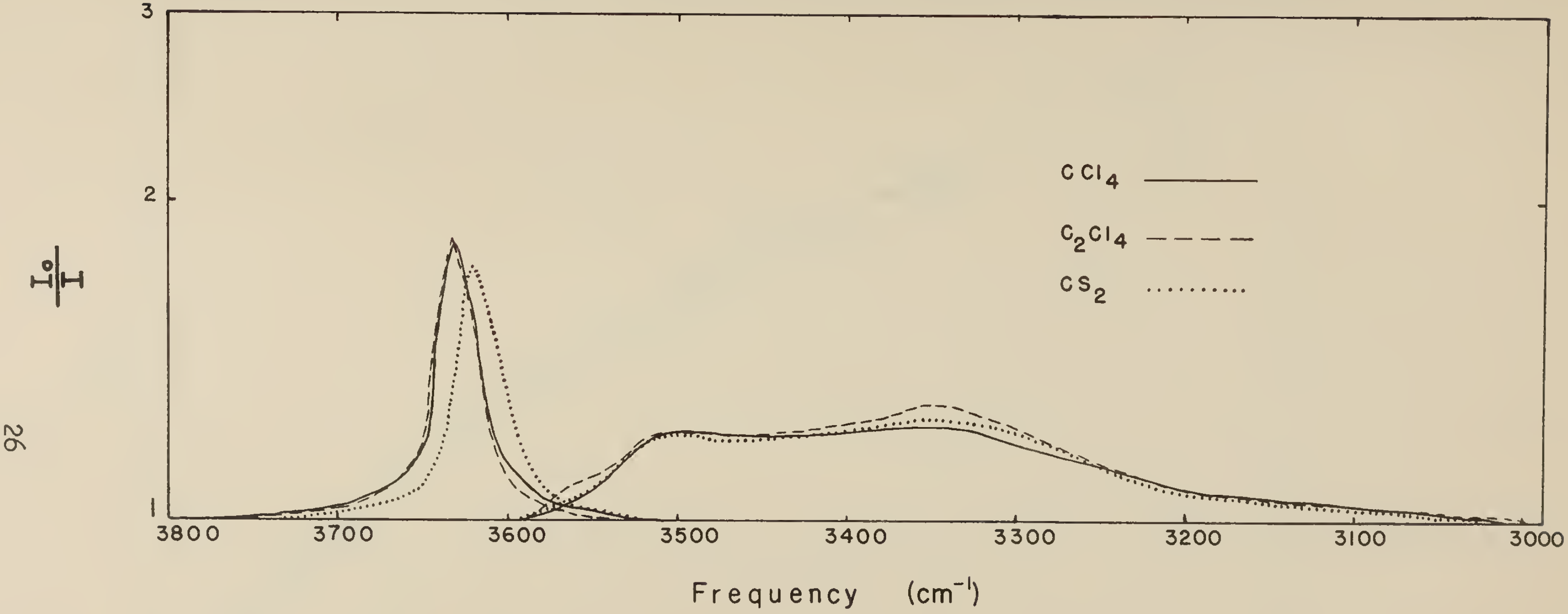


Figure 3

Optical Density versus Frequency

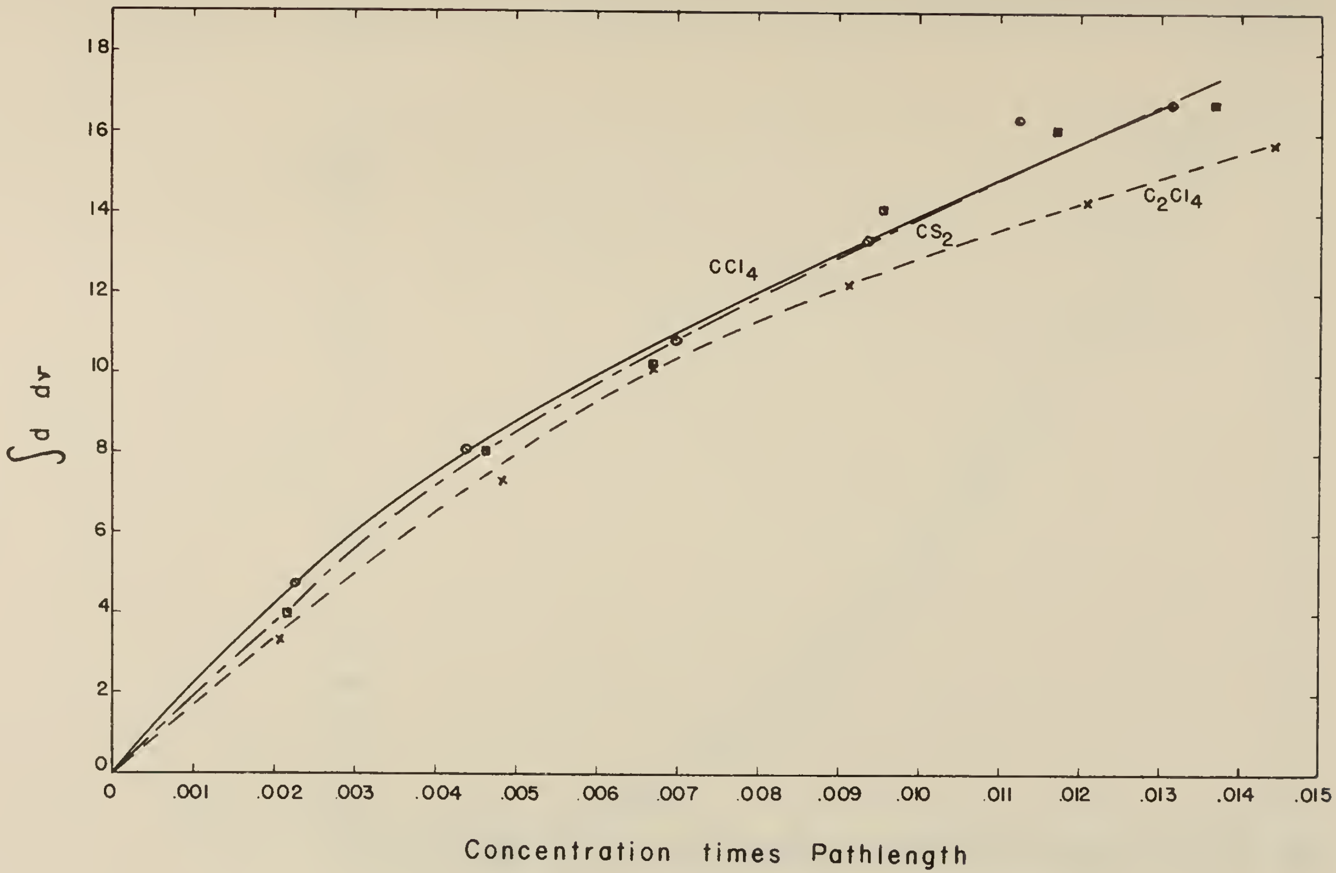


Figure 4

$\int d \, d\nu$ versus Concentration times Pathlength

Monomer Band

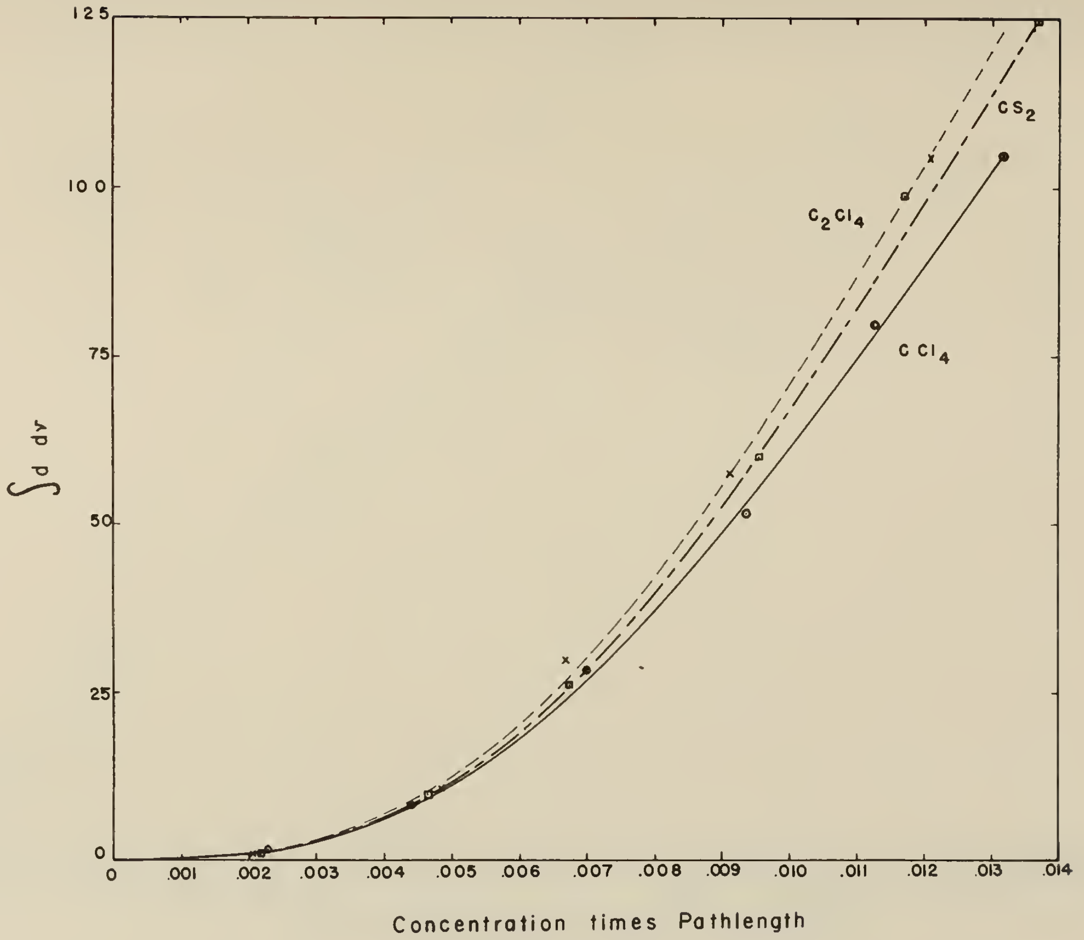


Figure 5

$\int d\,d\nu$ versus Concentration times Pathlength

Polymer Band

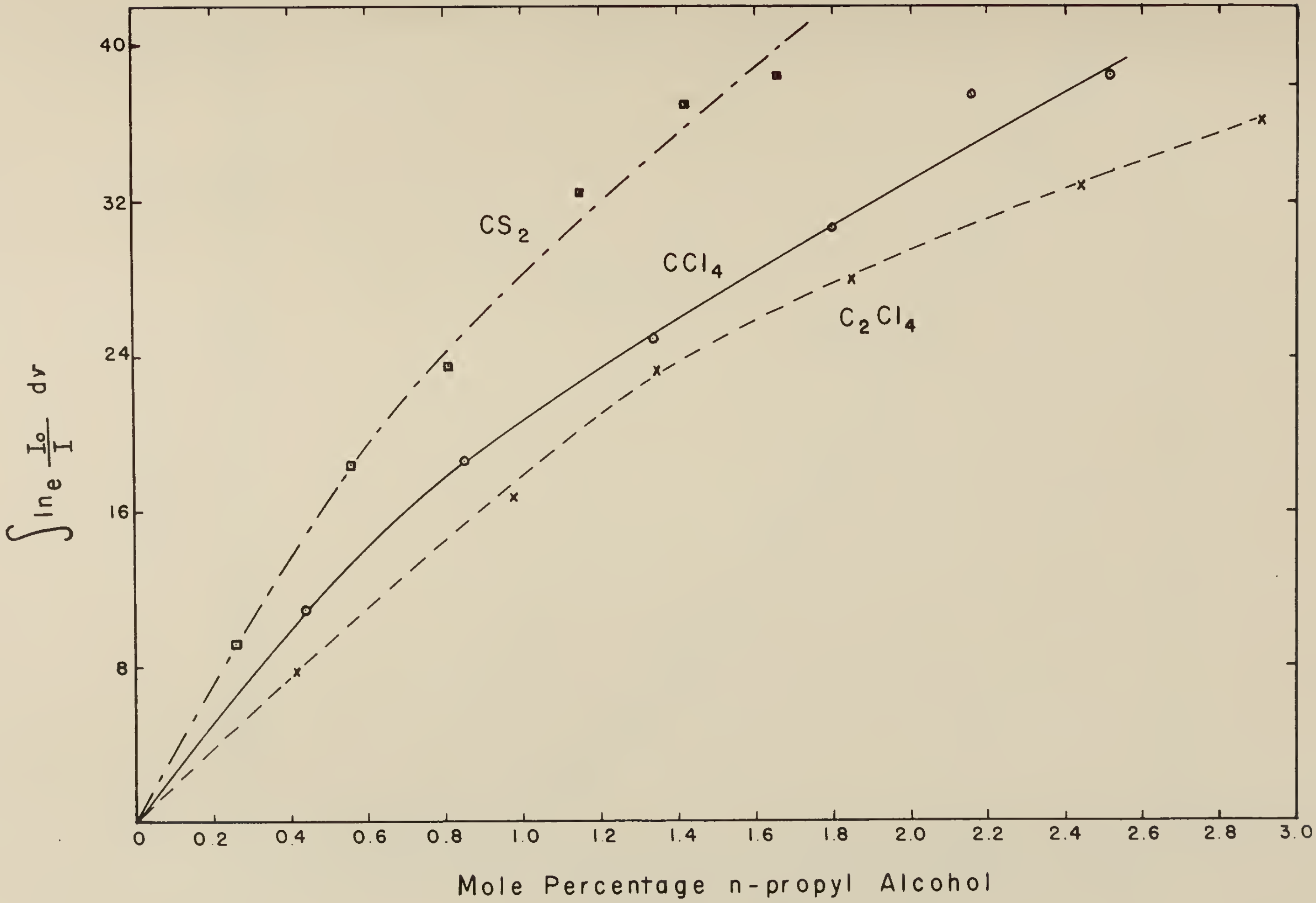


Figure 6

$\int \ln_e \frac{I_0}{I}\, d\nu$ versus Mole Percentage n-propyl Alcohol Monomer Band

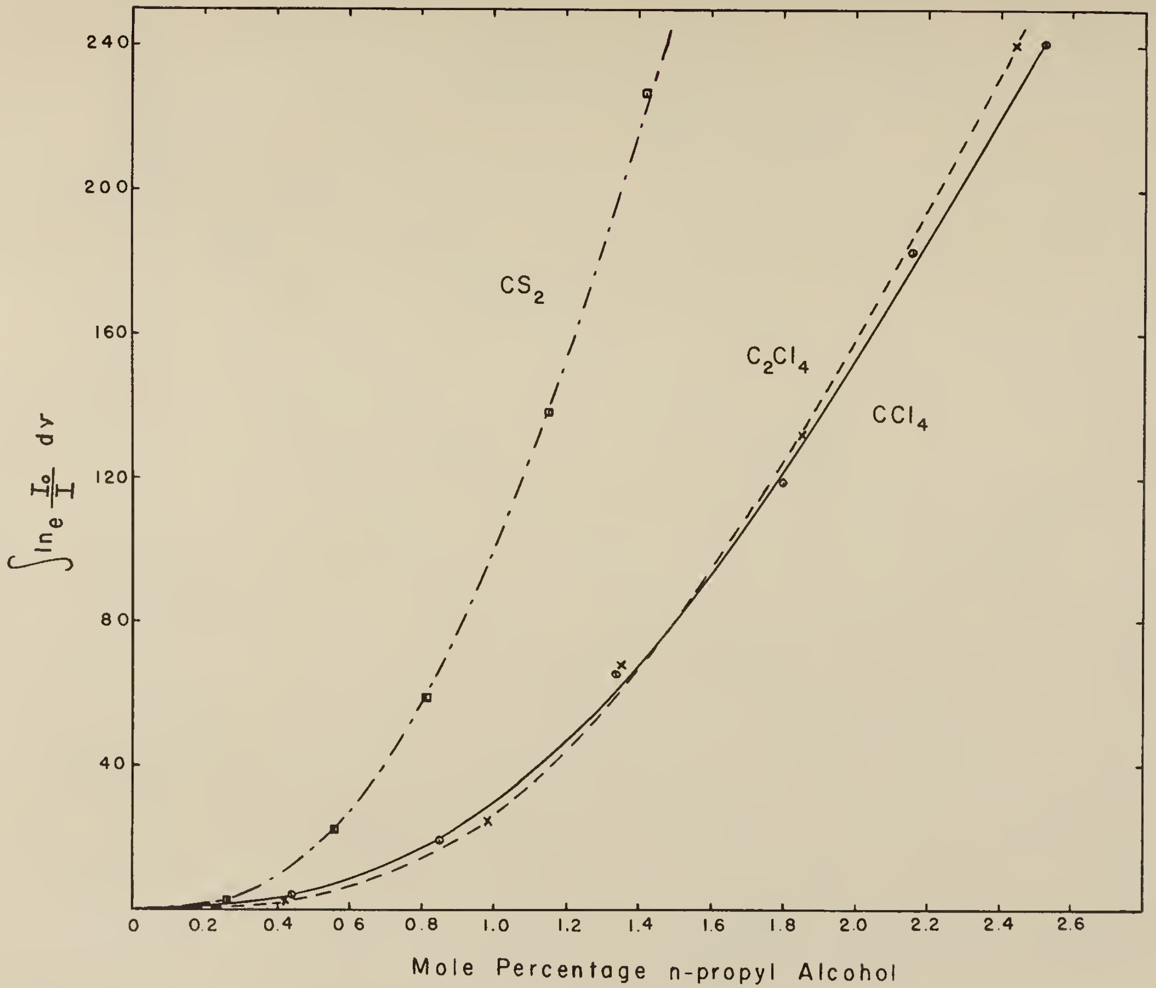


Figure 7

$\int \ln_e \frac{I_o}{I} d\nu$ versus Mole Percentage n-propyl Alcohol Polymer Band

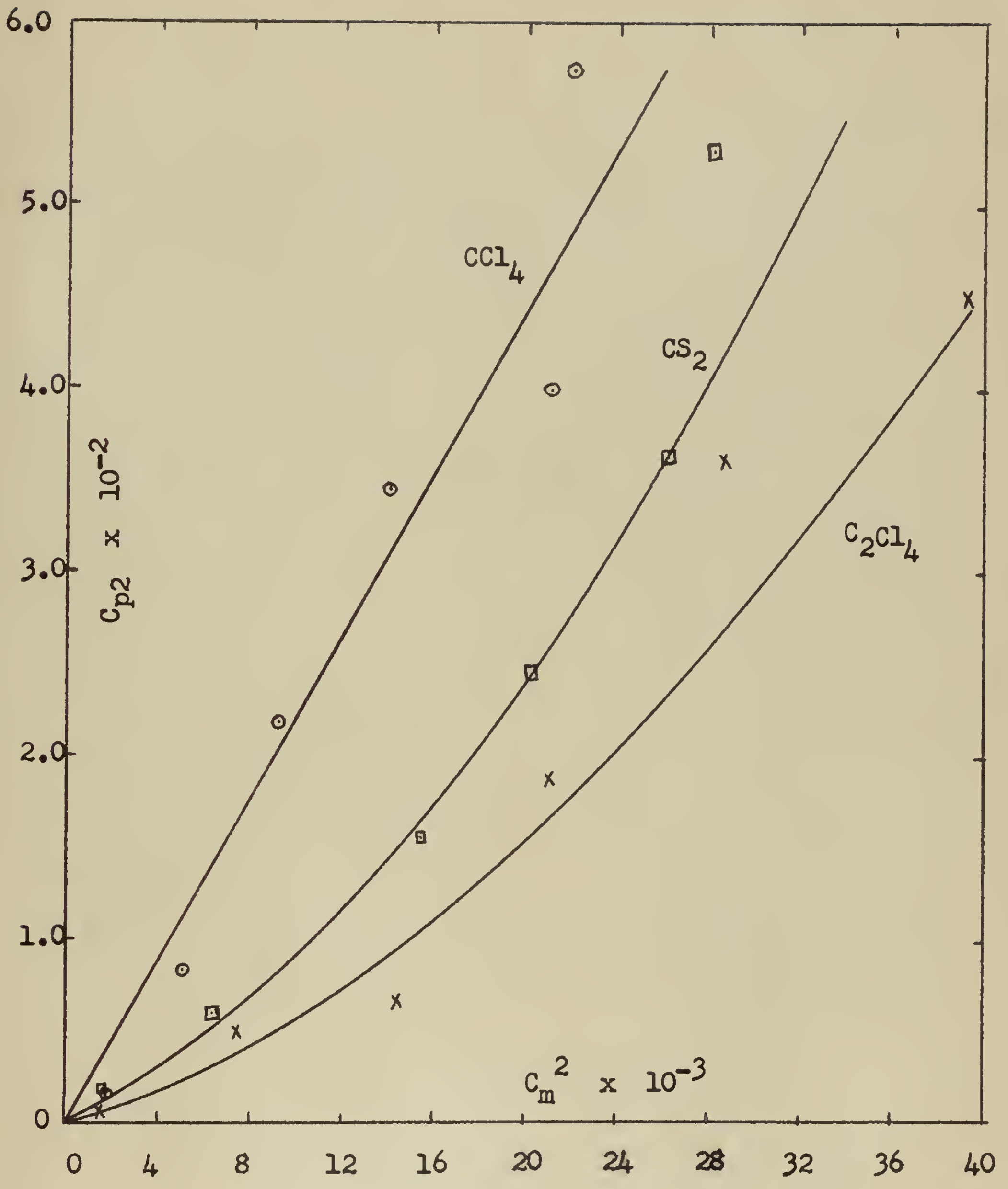


Figure 8

Monomer-Dimer Equilibrium Reactions

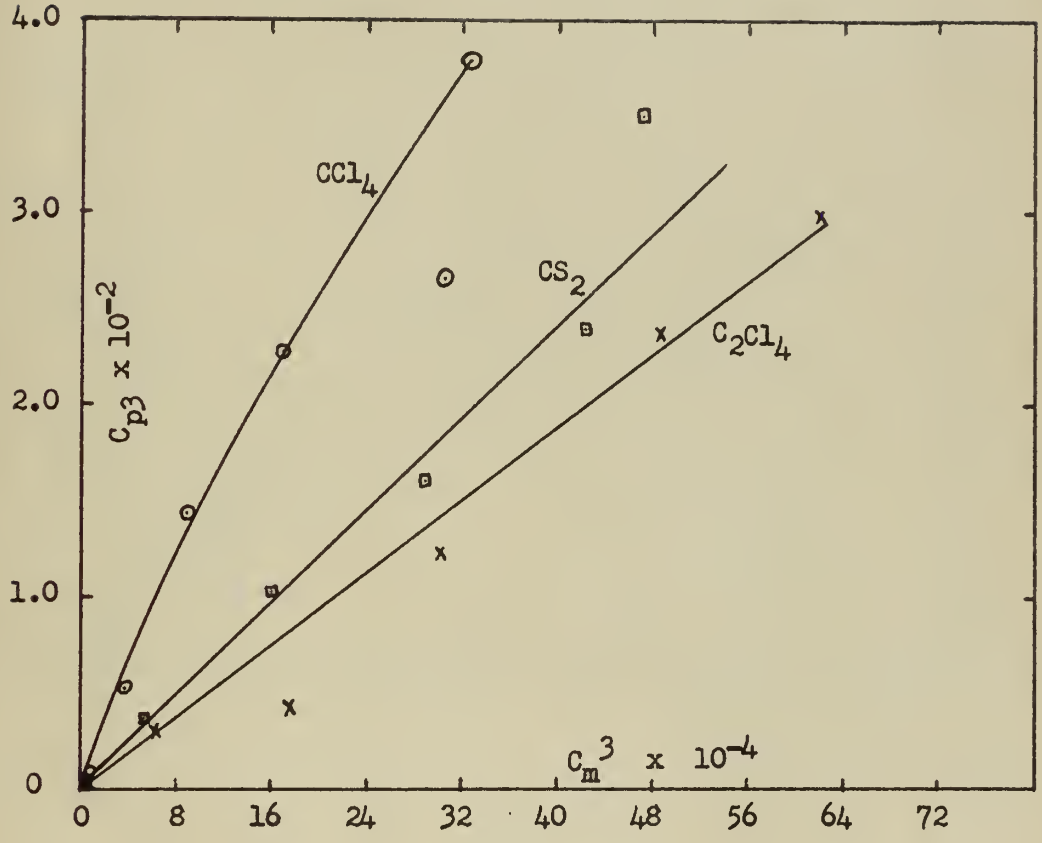


Figure 9

Monomer-Trimer Equilibrium Relationships

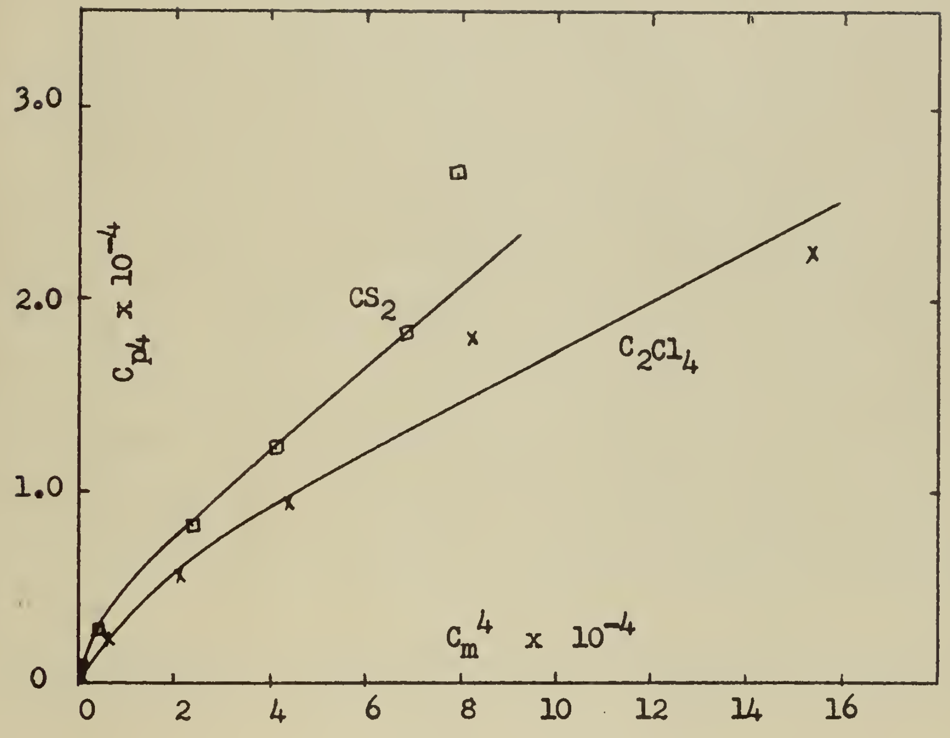


Figure 10

Monomer-Tetramer Equilibrium Relationships

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